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June 29, 2006

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RETURN RECEIPT REQUESTED

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SUBJECT: CONOCOPHILLIPS WOOD RIVER REFINERY; CIVIL ACTION NO. H-05-0258,  
PARAGRAPH 210

Dear Sir or Madam:

Pursuant to paragraph 210 of the Consent Decree United States of America and the States of Illinois, Louisiana, and New Jersey, Commonwealth of Pennsylvania and the Northwest Clean Air Agency v. ConocoPhillips Company, Civil Action No. H-05-0258, entered by the District Court for the Southern District of Texas on January 27, 2005, ConocoPhillips Wood River Refinery (WRR) is submitting the attached Benzene Waste NESHAP Sampling Plan. Also attached are two corrected pages to the Benzene Waste NESHAP Compliance Review and Verification Report. Please replace these pages in this report which was submitted to you on May 26, 2006.

Please contact Jay Rankin at 618-255-2737 with any questions.

Sincerely,

Neal Sahni  
Team Leader - Environmental

Attachments

**BENZENE WASTE OPERATIONS  
SAMPLING PLAN  
(6BQ COMPLIANCE OPTION)  
CONOCOPHILLIPS COMPANY  
WOOD RIVER REFINERY, ROXANA, ILLINOIS**

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**June 28, 2006**

**Project #: 436-020-001**

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**SUBMITTED BY: ConocoPhillips Company, Wood River Refinery**

**900 S. Central, Roxana, Illinois 62084**

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# 1.0 INTRODUCTION

ConocoPhillips Company (COP) operates a petroleum refinery in Roxana, Illinois, known as the Wood River Refinery (Refinery). The crude oil throughput for the Refinery is approximately 300,000 barrels per day. The Refinery produces gasoline, kerosene, diesel, residual fuel oil, asphalt, aviation jet fuel, liquid petroleum gas (LPG), and sulfur.

COP has entered into a Consent Decree (Consent Decree) with the U.S. Environmental Protection Agency (EPA) and several state agencies where COP operates refineries. The Consent Decree requires that COP conducts quarterly sampling at the Refinery for the purpose of calculating quarterly, uncontrolled benzene quantities in order to verify compliance with the Benzene Waste Operations National Emission Standards for Hazardous Air Pollutants (NESHAP [BWON]) regulation. As part of this requirement, COP must prepare and submit to the EPA a Benzene Waste Operations Sampling Plan (Plan). The Plan is designed to identify the quarterly benzene quantity of uncontrolled waste streams.

As set forth in Section N, Paragraph 211 of the Consent Decree, the Plan for the Refinery must include:

- All uncontrolled waste streams that count towards the treat-to-a target benzene quantity of 6 megagrams (Mg) per year (yr; 6BQ) calculation and contribute greater than 0.05 Mg/yr of benzene to the Refinery's Total Annual Benzene (TAB)
- The proposed sampling locations and methods for flow calculations to be used in calculating projected quarterly and annual benzene quantity calculations under the terms of Paragraph 214

This Plan addresses the requirements of the Consent Decree, Section N, Paragraph 209. The objective of this Plan is to provide procedures for obtaining benzene-containing waste samples that will be used to verify compliance with the 6BQ compliance option, in addition to TAB verification. The Plan includes procedures, quality assurance /quality control (QA/QC) protocol, scheduling, and methodology to ensure the accuracy of collected data. The Plan details the following:

- Sample locations and methods for flow calculations
- Sampling methodology
- Sample preservation and shipment

- QA/QC protocol
- Health and safety considerations
- Contingency procedures

Additionally, Section N, Paragraph 212 of the Consent Decree requires that the Refinery implement sampling, as presented in this Plan, during the first full calendar quarter after submittal. The Consent Decree further specifies that Wood River will continue to adhere to the Plan unless and until EPA disapproves of the Plan, or if the Plan is modified, with EPA's approval, as specified below.

If changes in processes, operations, or other factors lead Wood River to conclude that the existing Plan no longer provides an accurate basis for estimating the Refinery's quarterly or annual benzene quantities, Wood River may submit a Revised Sampling Plan (Revised Plan). The Revised Plan must be submitted no later than 90 days after Wood River determines that the original Plan no longer provides an accurate accounting of uncontrolled benzene waste.

Wood River may request to modify the Plan 2 years after implementation. Wood River may submit a request to the EPA for approval to revise the Refinery's Plan. This request may include reducing frequency by which samples are collected and sampling locations. However, Wood River cannot implement the Revised Plan until it is approved by the EPA.

## **1.1 COMPLIANCE OPTION**

Wood River has opted to use the compliance option listed under 40 CFR 61.342(e), otherwise known as the 6BQ option. This compliance option allows the Refinery to generate and manage up to 6.0 Mg/yr of uncontrolled benzene as waste.

## **1.2 TAB REPORTING**

The Wood River Refinery's Revised 2004 TAB quantity was estimated at 101.27 Mg. Of the 101.27 Mg, 3.66 Mg of benzene contributed towards the Revised 6BQ. The revised TAB and BQ was estimated based on refinery knowledge, maintenance practices, and waste stream sampling, and was verified by the Benzene Waste NESHAP Review and Verification Report submitted May 26, 2006.

### **1.3 TAB VERIFICATION**

At the end of each quarter, Wood River will calculate a quarterly and projected annual uncontrolled benzene quantity for the Refinery based on sampling results and approved flow calculations. Wood River will use the average of a minimum of three samples collected for each end-of-line (EOL) sample in these calculations. These calculations will be submitted in quarterly reports. If the quarterly reports identify potential violations then the Contingency Plan outlined in Section 6.0 of this Plan will be followed.





## **2.0 WASTE HANDLING SYSTEMS**

### **2.1 PROCESS SEWER**

The process sewer is used to collect and convey wastewater from throughout the Refinery to the WWTP. The process sewer is not controlled in accordance with BWON standards. The process sewer conveys wastewater to the Lower Lift Station at the head of the WWTP. Process sewers at WWTP (including Site 9.5) are controlled according to BWON standards.

In addition to the Process Sewer, the Refinery uses an above ground pressurized line to convey high benzene-containing, high flow wastewater streams to the WWTP. This line is known as the NESHAP Header. The main purpose of the NESHAP Header is to convey desalter water to the WWTP.

### **2.2 SPENT CAUSTIC SYSTEM**

Some spent caustic that is generated by the Refinery is simply drained to the uncontrolled process sewer. Other spent caustic streams are routed to the Spent Caustic System. Waste that is sent to the Spent Caustic System first enters Tank CH-278. CH-278 is equipped with a fixed-roof cover and a closed-vent system which routes vapors to the WWTP Flare. From CH-278, spent caustic is metered into the Upper Lift Station of the WWTP for pH control.

### **2.3 WASTEWATER TREATMENT PLANT (WWTP)**

Wastewater is conveyed by the process sewer to the Lower Lift Station at the front end of the WWTP. The Lower Lift Station also receives waste from vacuum trucks. The Lower Lift Station is covered and equipped with a closed-vent system that routes vapors to the WWTP Flare. From the Lower Lift Station, wastewater is pumped to the Upper Lift Station. Desalter water from the three distillation units is pumped to the Upper Lift Station through the controlled NESHAP Header. The Upper Lift Station is covered and equipped with a closed-vent system that routes vapors to the WWTP Flare.

From the Upper Lift Station, wastewater is sent through a series of corrugated plate interceptors (CPIs). Oil is skimmed from the CPIs and sent to Tank B-121. Oil from B-121 is pumped to the "D Tanks" (described below), while water is sent back to the Lower Lift Station. Water flows out of the CPIs to the Air Disengager. Sludge is periodically removed from the CPIs to an uncontrolled dumpster. The CPIs, Tank B-121, and the Air Disengager are equipped with fixed-roof covers and closed-vent systems that route vapors to the WWTP Flare.



From the Air Disengager, water is sent to dissolved nitrogen floatation (DNF) units. Sludge is periodically removed from the DNFs to the uncontrolled dumpster. Oil is skimmed to the "D Tanks", while water is sent to the DNF Effluent Sump. The DNFs and DNF Effluent Sump are equipped with fixed-roof covers and closed-vent systems that route vapors to the WWTP Flare.

From the DNF Effluent Sump, water is sent to the Equalization Diversion Tank. This tank is equipped with an external floating-roof cover. Oil can be skimmed from the Equalization Diversion Tank to the "D Tanks". Water from the Equalization Diversion Tank then flows to the SBT Floc Basin, Staged Biotreater, Pond 2, and secondary clarifiers. The treatment train from the Equalization Diversion Tank to the secondary clarifiers are designed and operated as EBUs in accordance with BWON standards. Finally, treated wastewater is discharged to effluent lagoons in accordance with applicable permit requirements.

The "D Tanks" consist of tanks D-52, D-53, and D-54. Each tank is equipped with a fixed-roof cover and a closed-vent system that routes vapors to the WWTP Flare. Tank D-52 receives recovered oil from the sludge handling process (described below). Tank D-53 receives oil from Tank B-121 and the Equalization Diversion Tank. Tank D-54 receives oil skimmed from the DNFs. Water is drained from all of these tanks back to the Lower Lift Station. Oil from these tanks is pumped to Tank F-21. Sludge is periodically removed from these tanks and sent to the sludge handling process.

Tank F-21 receives recovered oil from the "D Tanks", groundwater recovery operations, MDO systems, oil skimmed from the Sour Water System, and miscellaneous waste streams via vacuum truck. Recovered oil is pumped from F-21 to the distillation units as feed. Water is drained to Tanks F-68 and F-72 upstream of the Sour Water System. Tanks F-21, 68, and 72 are equipped with internal floating roof covers.

## **2.4 SLUDGE PROCESSING**

Sludge recovered from CPIs, DNFs, "D Tanks", and tank cleaning activities is stored in Tanks C-63 and 64 at the head of the sludge processing train. Tanks C-63 and 64 are equipped with fixed-roof covers and closed-vent systems that route vapors to the WWTP Flare. From C-63 and 64, sludge is pumped to centrifuges. Solids are separated from liquids in the centrifuges. Solids are sent to a hopper while liquids are sent to Drum V-5300. The centrifuges, hopper, and V-5300 are all equipped with closed-vent systems that route vapors to the WWTP Flare.



From the hopper, solids are removed to an uncontrolled mix tank. Vacuum trucks move the material from the mix tank for processing by the Coker. Liquids from V-5300 are sent to Tank D-52.

## **2.5 MAINTENANCE DROP OUTS (MDOs)**

Many of the process units at the Refinery utilize MDOs to manage waste. For the most part, these MDOs are equipped with closed-vent systems that route vapors to one of a number of flares. Typically, MDOs are emptied by vacuum truck.

## **2.6 SOUR WATER SYSTEM**

Sour water generated by various units in the Refinery is collected in one of two feed surge vessels. These vessels are equipped with closed-vent systems that route vapors to a flare. One vessel feeds the DU-2 Sour Water Stripper; the other feeds the Gas Plant Sour Water Stripper. Oil skimmed from the DU-2 Feed Surge Vessel is sent to the Flashed Tops Accumulator (on vacuum), and then to the LFD Accumulator (on flare). Water is drained from the LFD Accumulator and is used as DU-2 desalter make-up water. Oil from the LFD Accumulator is sent back into the unit for reprocessing. Water from the DU-2 Sour Water Stripper is used as desalter make-up water. Overhead from the Stripper is vented to the Gas Plant MDO (on flare).

Oil skimmed from the Gas Plant Feed Surge vessel is drained to the GAS Plant MDO. Some of the stripped water from the Gas Plant Stripper is sent to the process sewer and some is used as desalter make up-water. Overhead from the Gas Plant Stripper is gathered in the Sulfur Recovery Unit (SRU) Sour Water Accumulator. Oil is skimmed from this accumulator and routed back to the Gas Plant MDO. Water is pumped from the Accumulator to the SRU Sour Water Stripper. Stripped water is sent to the Lower Lift Station at the WWTP. Stripper overhead is directed to the Sulfur Recovery Unit.



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## 3.0 SAMPLE LOCATIONS

The purpose of the Plan is to verify and track the Refinery's status with regard to the 6BQ compliance option. This is accomplished through the quarterly collection and analysis of aqueous and organic samples both at the EOL and point of generation (POG) for those waste streams that contribute greater than 0.05 Mg of benzene to the BQ. EOL sampling points have been identified that either quantify significant benzene-containing waste streams or will verify the absence of benzene in waste handling systems that receive high volumes of waste. Waste streams that are not conveyed in controlled individual drain systems or treated in controlled waste management units will require quantification.

Wood River is also required to sample uncontrolled waste streams that contribute to the 6BQ and contain greater than 0.05 Mg/yr of benzene to the Refinery's TAB.

### 3.1 END-OF-LINE SAMPLING

As part of the quarterly calculation of the 6BQ required by the Consent Decree, Wood River will use the EOL sampling data to verify compliance with the 6BQ compliance option. Figure 1 shows the EOL locations on a waste/slop/off-spec oil management schematic for the Refinery. Table 1 summarizes the sample points and the methods for flow determination for each stream contributing to the 6BQ. The EOL locations are as follows:

- Dock Sumps / CH-210
- MP Groundwater
- Distilling West Process Sewer Sump
- Lower Lift Station
- Mix Tank
- Dumpster

A minimum of three representative samples will be collected from each EOL location on a quarterly basis. The average of the results will be used to calculate the quarterly and projected annual uncontrolled benzene quantity.

### **3.1.1 DOCK SUMPS / CH-210**

There are four docks used for barge loading. Material loaded at the dock includes asphalt, fuel oil, slurry oil, gas oil, naphtha, benzene, diesel, and aviation fuel. Some loading of gasoline and gasoline blending components also occurs.

There are four uncontrolled sumps associated with the barge loading docks. There is one sump for each dock. These sumps receive rain water and organic material that drips from loading lines. The sumps are pumped to CH-210.

Therefore, the EOL will be Tank CH-210. This EOL sampling location will verify the benzene concentration of waste from dock activities for quarterly and annual 6BQ calculations. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration.

### **3.1.2 MP (MAIN PLANT) GROUNDWATER**

Benzene in groundwater is exempt from inclusion in the TAB. However, benzene in uncontrolled groundwater must be included in the 6BQ. The Refinery does manage some groundwater in uncontrolled waste management units.

Water from Well 83 (Main Plant) is pumped directly to the Cooling Water Treater. Thus, only water from Well 83 needs to be counted in the Refinery's 6BQ. Because the water is pumped directly to the Cooling Water Treater, the effluent of Well 83 is the first uncontrolled waste management unit and therefore an EOL.

The MP Groundwater EOL sampling location will verify the benzene concentration of the water recovered from Well 83 for quarterly and annual 6BQ calculations. This EOL sample will be collected at the well pump discharge. Aqueous samples will be collected and analyzed for benzene concentration.

In the event that this well is removed from service this EOL sampling location will be eliminated as an EOL location.

### **3.1.3 DISTILLING WEST PROCESS SEWER SUMP**

Distilling West consists of a Crude Unit, Vacuum Unit, and Coker. The Distilling West process sewer is uncontrolled with respect to the BWON rule. Excluding Desalter effluent, most waste streams are managed by the process sewer. Desalter water is conveyed to the Wastewater Treatment Plant via the controlled NESHAP Header. The EOL sampling for the Distilling West will verify the benzene concentration of wastewater from the units listed above for quarterly and annual 6BQ calculations. This EOL sample will be taken at the effluent of the sump that pumps the water to the Upper Lift Station located in the Main Refinery. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration.



#### **3.1.4 LOWER LIFT STATION**

The process sewer is used to collect and convey wastewater from throughout the Main Refinery to the wastewater treatment plant (WWTP). The process sewer is not controlled in accordance with BWON standards. The process sewer conveys wastewater to the Lower Lift Station at the head of the WWTP.

The Influent to the Lower Lift Station EOL sample will verify the benzene concentration of wastewater from the Main Refinery units for quarterly and annual 6BQ calculations. This EOL sample will be taken at the pump discharge to the Upper Lift Station. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration.

#### **3.1.5 MIX TANK**

From sludge storage tanks C-63 and 64, sludge is pumped to centrifuges. Solids are separated from liquids in the centrifuges. Solids are sent to a hopper while liquids are sent to Drum V-5300. From the hopper, solids are removed to an uncontrolled mix tank. Vacuum trucks move the material from the mix tank for processing by the Coker.

To the extent that it represents double counting in the EOL calculations, the benzene analytical results from the Dumpster EOL (see section 3.1.6) will be subtracted from the Mix Tank benzene analytical results.

The Mix Tank EOL sample will verify the benzene concentration of sludge stored in this tank for quarterly and annual 6BQ calculations. This EOL sample will be taken at the tank prior to the sludge being sent to the Coker. Solids will be collected and analyzed for benzene concentration.

#### **3.1.6 DUMPSTER**

From the Air Disengager in the WWTP, water is sent to dissolved nitrogen floatation (DNF) units. Sludge is periodically removed from the DNFs and CPIs to the uncontrolled Dumpster. Oil is skimmed to the "D Tanks", while water is sent to the DNF Effluent Sump.

The Dumpster EOL sample will verify the benzene concentration of sludge stored in the dumpster for quarterly and annual 6BQ calculations. This EOL sample will be taken at the dumpster prior to the sludge being routed to the "D Tanks". All phases (if available) will be collected and analyzed for benzene concentration.

In the event that the dumpster is removed from service, this EOL sampling location will be eliminated as a EOL location.

### **3.2 UNCONTROLLED WASTE STREAMS CONTRIBUTING GREATER THAN 0.05 MG/YR BENZENE**

Several uncontrolled waste streams were identified as contributing greater than 0.05 Mg/yr benzene to the Revised 6BQ. Table 1 summarizes the sampling points and the method for flow rate determination for each stream contributing greater than 0.05 Mg/yr of benzene to the Revised 6BQ. These streams are as follows:

- SRC Column Water Boot (BEU)
- Surge Drum and Charge Pump Sample Station (CR3)
- Sour Water Stripper Bottoms (Hub#37) (LOT)
- Outlet Sample Bleeder Sample Station (LOT)
- Sample Bleeder Sample Station (LOT)
- Second Stage Triline Samples (DU1)
- First Stage Triline Samples (DU1)
- Mixed Crude Desalter Triline Samples (DU2)
- Distilling West Desalter (1841) Triline
- Distilling West Desalter (1840) Triline
- Sour Water Stripper Bottoms (Environmental Operations)
- Miscellaneous Vacuum Truck Hose Drillage To F21 Sump (PPL)
- Gasoline Sampling (Motor Laboratory)
- Dock Waste Permits (Dock)
- Main Property Well W-83 (Spills and Miscellaneous Waste Streams)
- Solid Waste

These waste streams are required to be sampled quarterly. The basis of inclusion for each of these uncontrolled waste streams is provided in the following sections.

### **3.2.1 SCR COLUMN WATER BOOT (BEU)**

It is estimated that the SCR Column Water Boot in the Benzene Extraction Unit (BEU) contributes 0.22 Mg/yr benzene towards the Revised 6BQ. This POG contributes to the Revised 6BQ because it drains to the uncontrolled process sewer. This sample will be collected at the effluent of the SCR Column Water Boot prior to entering the process sewer. Aqueous samples will be collected and analyzed for benzene concentration.

### **3.2.2 SURGE DRUM AND CHARGE PUMP SAMPLE STATION (CR3)**

It is estimated that the Surge Drum and Charge Pump sample station contributes 0.07 Mg/yr of benzene to the Revised 6BQ. This POG contributes to the Revised 6BQ because it drains to the uncontrolled process sewer. This sample will be collected where the waste stream enters the process sewer. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration.

### **3.2.3 SOUR WATER STRIPPER BOTTOMS (CGP-LOT)**

This waste stream, Sour Water Stripper Bottoms (Hub #37) is estimated to contribute 0.07 Mg/yr of benzene to the Revised 6BQ. This sample will be collected where the waste stream enters the process sewer. The aqueous phase will be collected and analyzed for benzene concentration.

### **3.2.4 OUTLET SAMPLE BLEEDER SAMPLE STATION (CGP-LOT)**

This sample station waste stream is estimated to contribute 0.05 Mg/yr of benzene to the 6BQ. This sample will be collected where the waste stream enters the process sewer. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration.

### **3.2.5 SAMPLE BLEEDER SAMPLE STATION (CGP-LOT)**

This sample station waste stream is estimated to contribute 0.05 Mg/yr of benzene to the Revised 6BQ. This sample will be collected where the waste stream enters the process sewer. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration.



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### **3.2.6 SECOND STAGE TRILINE SAMPLES (DU1)**

It is estimated that the Second Stage Desalter Triline sample contributes 0.16 Mg/yr of benzene to the Revised 6BQ. Quarterly samples will be collected during a Triline sample event for the Second Stage Desalter. Both aqueous and organic phases will be collected and analyzed for benzene concentration.

### **3.2.7 FIRST STAGE TRILINE SAMPLES (DU1)**

It is estimated that the First Stage Desalter Triline sample contributes 0.06 Mg/yr of benzene to the Revised 6BQ. Quarterly samples will be collected during a Triline sample event for the First Stage Desalter. Both aqueous and organic phases will be collected and analyzed for benzene concentration.

### **3.2.8 MIXED CRUDE DESALTER TRILINE SAMPLPES (DU2)**

It is estimated that the Mixed Crude Desalter Triline sample contributes 0.26 Mg/yr of benzene to the Revised 6BQ. Quarterly samples will be taken during a Triline sample event for the Mixed Crude Desalter. Both aqueous and organic phases will be collected and analyzed for benzene concentration.

### **3.2.9 DISTILLING WEST DESALTER (1841) TRILINE**

It is estimated that the Distilling West Desalter (1841) Triline sample contributes approximately 0.26 Mg/yr of benzene to the Revised 6BQ. Quarterly samples will be taken during a Triline sample event for the Distilling West Desalter (1841). Both aqueous and organic phases will be collected and analyzed for benzene concentration.

### **3.2.10 DISTILLING WEST DESALTER (1840) TRILINE**

It is estimated that the Distilling West Desalter (1840) Triline sample contributes 0.26 Mg/yr of benzene to the Revised 6BQ. Quarterly samples will be taken during a Triline sampling event for the Distilling West Desalter (1840) Triline. Both aqueous and organic phases will be collected and analyzed for benzene concentration.

### **3.2.11 SOUR WATER STRIPPER BOTTOMS (ENVIRONMENTAL OPERATIONS)**

It is estimated that the Sour Water Stripper Bottoms contributes 0.09 Mg to the Refinery's Revised 6BQ. Quarterly samples will be collected where the waste stream enters the process sewer. The aqueous phase will be collected and analyzed for benzene concentration.



### **3.2.12 MISCELLANEOUS VACUUM TRUCK HOSE DRIPPAGE TO F21 SUMP (PPL)**

This waste stream is uncontrolled because this stream is routed to an uncontrolled F21 sump. Based on the Revised TAB, it is estimated that this waste stream contributes 0.08 Mg/yr of benzene to the 6BQ. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration. This sample will be collected from a bleeder on the discharge of the sump pump.

### **3.2.13 GASOLINE SAMPLING (MOTOR LABORATORY)**

Laboratory personnel also discard approximately 10 to 12 gallons of gasoline samples each day to the uncontrolled pipeline sump. It is estimated that this activity generates 0.09 Mg of benzene as waste each year. A sample of the laboratory waste will be collected from the pipeline sump. Both aqueous and organic phases (if possible) will be collected and analyzed for benzene concentration.

### **3.2.14 DOCK WASTE PERMITS (DOCK)**

The Dock waste streams listed in the Revised TAB that contribute greater than 0.05 Mg are vacuum truck shipments of CH-210 Gasoline/Water and CH-210 Gasoline, to various refinery waste disposal sites. The benzene concentration of these streams is based on Waste Permits and engineering estimates. This material is usually pumped to Tank CH-210, but the lines connecting the sumps to CH-210 were out of service during the onsite verification and review. The waste streams comprise the same waste that is to be sampled in the CH-210 EOL location. Therefore, benzene concentrations for Dock Waste Permits will be obtained from the EOL samples collected at Tank CH-210.

### **3.2.15 MP WELL W-83 (SPILLS AND MISCELLANEOUS WASTE STREAMS)**

It is estimated that the well W-83 POG contributes 0.73 Mg/yr of benzene to the Revised 6BQ. Because this waste stream contributes greater than 0.05 Mg/yr of benzene to the 6BQ, it is required to be sampled quarterly. This POG is also an EOL sampling location. Therefore the benzene concentration will be obtained from the analytical results of the MP Well W-83 EOL location.

### **3.2.16 SOLID WASTE**

Solid waste generated by Tank A-200 Clean Out contributes greater than 0.05 Mg/yr of benzene to the Revised 6BQ. Because this stream is not routinely generated, it will be sampled as described in Section 3.3. Solids will be collected and analyzed for benzene concentration.



DNF Bottoms/CPI Solids contributes greater than 0.05 Mg/yr of benzene to the Revised 6BQ as well. This waste is the same as the waste sampled at the Dumpster EOL location. Therefore, the benzene concentration will be obtained from the analytical results of the Dumpster EOL location.

### **3.3 NON-ROUTINE SAMPLES**

Non-routine samples may be the result of process requirements, turnaround events, hydrocarbon spills, tank cleaning (e.g. Tank A-200), remediation activities, or waste disposal. Non-routine samples do not include the EOL or greater than 0.05 Mg/yr samples described earlier. During the reporting period the need may arise to collect non-routine samples which will be used for calculating the annual TAB or uncontrolled benzene quantity. These samples may not necessarily be collected or reported in accordance with the BWON or Consent Decree requirements.

### **3.4 WASTE STREAM FLOW ESTIMATES**

Waste stream flow rates and volumes for the sample locations will be based on one or more of the following:

- Engineering estimates
- Operations personnel interviews
- Flow meter readings
- Direct measurements
- Process knowledge
- Vessel size
- Pumping cycles
- Waste manifests or transfer permits

Table 1 summarizes the method used to determine the waste stream flow rates.



**Trihydro**

## 4.0 SAMPLING PROCEDURES

The variety of waste streams and locations to be sampled will require different sampling techniques. Each location's sampling technique is listed in Table 1. The recommended sampling technique will be via a condensing cooler in accordance with United States EPA (USEPA) Method 25D. Where sampling through a condensing cooler is deemed impractical, samples will be collected in a manner that minimizes volatilization of organic compounds consistent with USEPA Method 25D. This procedure is referred to as "grab sampling" in the Plan. The Refinery will use the following techniques for each sample group:

- Cooler Sampling – Cooler samples will be collected in a condensing cooler equivalent to USEPA Method 25D. The sample cooler consists of a stainless steel cooling coil. Prior to sample collection, ice will be placed in the cooler to chill the sample to less than 10 degrees Celsius (C).
- Grab Sampling – Where cooler sampling is not practicable, samples will be collected in a manner that minimizes the loss of volatile organic compounds (VOCs). Some grab samples will be collected in a disposable bailer, wide-mouth jar, or other type of sample container. Aqueous and organic samples will then be transferred from the bailer or other type of sample container to 40 (milliliter) mL Volatile Organic Analysis (VOA) vials. Solid waste will be collected and transferred in wide-mouth jars provided by the laboratory. Other grab samples may not require the use of a bailer, wide-mouth jar, or other type of sample container. In this case, the sample container may be directly filled from a sample tap or valve.
- Non-Routine Samples – Non-routine samples will be collected as Grab Samples or Cooler Samples as necessary. Both aqueous and organic phases will be transferred to the laboratory in VOA vials, and solid samples (e.g., sludge, contaminated soil) will be transferred in wide-mouth jars.

At a minimum, three representative samples of each identified EOL waste stream will be collected during each quarterly sampling event.

Individuals tasked with the collection of samples described in this Plan will be trained to collect BWON samples. Individuals will complete annual refresher training.

### 4.1 COOLER SAMPLING PROTOCOL

A cooling coil and condensing cooler will be used as the sampling device for select sample locations listed in Table 1. As part of the sampling protocol, field procedures detailed in Section 4.3 will be used. The following routine will be adhered to when using this sampling methodology:



1. Notify operations in advance of anticipated sampling dates and times.
2. Prior to sampling, stagnant wastewater will be purged from the enclosed pipe.
3. The sample lines and cooling coil will be purged with at least four volumes of the waste stream.
4. The coil will be blocked in and the waste stream allowed to cool to less than 10 degrees C.
5. Prior to sample collection, verify the temperature of the waste stream exiting the condensing cooler is less than 10 degrees C.
6. Waste stream samples will be labeled and placed on ice for shipment to a qualified laboratory.
7. Sampling equipment will be decontaminated as described in Section 4.1.1.
8. Sample labels and chain-of-custody forms will be prepared as described in Section 4.3.

At the time of sample collection, the temperature of the waste stream will be recorded on the chain-of-custody form to demonstrate that the sample was cooled to less than 10 degrees C. If the temperature of the sample is greater than 10 degrees C, the collector will document why the sample could not be cooled to 10 degrees C. Any other discrepancies or occurrences that may impact sample integrity will be noted on the chain-of-custody form.

Samples will be collected in 40 mL VOA vials with Teflon-lined caps supplied by the laboratory. In accordance with SW-846, VOA vials will contain either an appropriate quantity of hydrochloric acid as required for aqueous samples or will be unpreserved for hydrocarbon samples.

#### **4.1.1 EQUIPMENT DECONTAMINATION**

The sampling cooler will be decontaminated before use and after each sample is collected. The decontamination procedure for the condensing cooler will include the following stages:

- Steam Cleaning – Each sample device will be loosely connected to a low-pressure steam source and purged with steam for at least 5 minutes. Steam insures the volatilization of most hydrocarbons that may be contained within the sampling train.
- Detergent Wash – Each sampling device will be connected to a reservoir containing a biodegradable detergent solution (e.g., Simple Green) and deionized or distilled water. This solution will be circulated through the sampling device using a peristaltic pump, or similar pump, for at least 5 minutes.



- Detergent Rinse – The detergent reservoir will be replaced with deionized or distilled water rinse. Water will be allowed to circulate through the sampling train for 5 minutes to remove any detergent residue.
- Acetone Rinse – Acetone will be pumped through the sampling train to remove any trace organic compounds. The acetone will be circulated through the sampling device for at least 5 minutes.
- Final Rinse – A final distilled/deionized water rinse will be performed. The final rinse will be allowed to circulate through the sampling train for at least 5 minutes.

As a check on the effectiveness of the decontamination procedure, an equipment blank will be collected from the sampling device for each cooler sampling event.

A sampling cooler may be dedicated to one sample location. If the sampling cooler is dedicated, decontamination is not required. In addition to sampling coolers, dedicated tubing will be used to connect the sampling cooler to the sample point. In some cases, hard pipe connectors may be used to facilitate the connection of the sampling cooler to the sample port. All hard pipe connectors will be dedicated or decontaminated prior to reuse.

## **4.2 GRAB SAMPLING PROTOCOL**

The Refinery may use grab sampling techniques for certain locations each quarterly reporting period. As part of the sampling protocol, field procedures detailed in Section 4.3 will be used. Samples will be collected via disposable bailers or other appropriate disposable sampling equipment. Each sample will be transferred to 40 mL VOA vials or other approved containers. Sampling equipment will be disposed of following the completion of each sampling event.

Sample locations listed in Table 1 may not require the use of disposable sample equipment. If this is the case, the waste stream sample will be collected directly in the sample container in a manner that minimizes exposure of the waste stream to the atmosphere. Stagnant waste will be drained from the piping leg or block valve before filling the sample containers.

## **4.3 FIELD PROCEDURES**

As part of the sample collection process (Sections 4.1 and 4.2), field procedures and sample handling protocol have been instituted to insure QA/QC, and to allow accurate determinations of benzene concentrations. These field procedures include field documentation that allow the sample collector to document critical information on the sampling procedure and the stream condition. The field procedures and sampling protocol also stipulate quality control procedures that allow sample results to be examined for accuracy and data reliability.



#### **4.3.1 SAMPLE HANDLING AND FIELD DOCUMENTATION**

Following sample collection, all sample containers and/or chain of custody reports will be labeled with the following information:

- Sample identification
- Name of collector
- Date and time of collection
- Place of collection
- Analysis
- Required preservatives
- Sample matrix
- Sample collection temperature

The 40 mL VOA vials will be placed in coolers on ice at the time of sampling. Samples will be sent to a COP-approved laboratory. Chain-of-custody forms will accompany each sample set submitted to the laboratory.

#### **4.3.2 BWON LABORATORIES**

COP completed an audit of the laboratory used by the Refinery to analyze BWON samples as required by the Consent Decree. The audit was conducted to ensure that proper analytical and QA/QC procedures are followed. If additional laboratories are required to be used, COP will perform a laboratory audit prior to the submittal of waste stream samples for benzene determination.

#### **4.3.3 LABORATORY ANALYSIS**

Waste stream samples will be analyzed by an audited, approved laboratory. In accordance with the BWON regulation, waste stream samples may be analyzed by USEPA Methods 8020, 8021, 8240, 8260, 602, or 624.

#### **4.3.4 FIELD QA/QC PROTOCOL**

The BWON regulation does not specify QA/QC protocol. However, the Refinery will establish a rudimentary QA/QC protocol. The Refinery's protocol will consist of the following:

- Collect one blind duplicate sample per 10 samples. Quality control samples will provide an evaluation of the analysis and precision of sample collection.
- Conduct sampling in order of lowest expected benzene concentration to highest expected benzene concentration to minimize carryover for cooler sampling.
- Request laboratory analysis per the chain-of-custody form.

#### **4.3.5 LABORATORY PROTOCOL**

The COP contract laboratory will have adequate QA/QC procedures in place to ensure the validity of analytical results. The Quality Assurance program will include management oversight of QA/QC procedures, internal accuracy and precision checks, external audits, and written guidelines and procedures concerning sample handling, recordkeeping, analytical methods, and calibration and maintenance of analytical equipment. Each laboratory's Quality Control program will detail procedures used to evaluate the accuracy and precision of analytical results.



## 5.0 HEALTH AND SAFETY CONSIDERATIONS

Sample collection personnel must meet all current safety requirements of the Refinery. The Refinery requires site-specific health and safety training before individuals are allowed on site. This training is conducted initially and requires refresher training to be completed as needed.

Individuals collecting samples must complete a safe work permit with the appropriate unit operators prior to sample collection. The collector must inform the operators of the sampler's task, locations of sampling points, and sampling procedures. The collector must not commence work until an authorized unit operator gives permission, and a work permit has been issued as required.

Hazards associated with sample collection can include exposure to benzene, rotating equipment, noise, eye and face exposure to hazardous chemicals, high temperatures and pressures, and exposure to hydrogen sulfide. Appropriate personal protective equipment (PPE) as required by the Refinery safety procedures will be used. Examples of PPE and personal exposure monitors to be worn by the sampler include:

- Fire-retardant clothing
- Hard hat
- Safety glasses
- Protective gloves
- Personal H<sub>2</sub>S monitor (where necessary)
- Hearing protection (where necessary)
- Appropriate footwear

## 6.0 CONTINGENCY PLAN

Wood River is required to use the quarterly sampling results for 6BQ verification. The sample results and flow estimates will be used to calculate a quarterly portion of the uncontrolled benzene quantity and a projected calendar year uncontrolled benzene quantity.

### 6.1 UNCONTROLLED BENZENE QUANTITY EXCEEDANCE

In the event that sample analysis indicates a higher benzene concentration than anticipated during normal operations, the following steps will be taken to ensure that the affected waste stream is properly represented in the quarterly 6BQ calculation.

- Review the sampling location to determine if the sample is representative of the waste stream.
- Review sample handling to assess the potential for contamination.
- Review the laboratory QA/QC to identify lab error or results outside of method/analytical limits.
- Review other factors that may influence the validity of the measured concentration.
- Analyze one or more additional samples to establish a representative benzene concentration. If more than one sample is analyzed, the average benzene concentration will be used.

### 6.2 CORRECTIVE MEASURES

If the quarterly uncontrolled 6BQ exceeds 1.5 Mg, or the projected annual uncontrolled benzene quantity equals or exceeds 6 Mg, then Wood River will undertake corrective measures provided that Wood River cannot identify reason(s) that result in exceedance of the 1.5 Mg limit. If Wood River can identify reason(s) and these reason(s) are not expected to reoccur, then Wood River may exclude the benzene quantity attributed to the identified reason(s) from the projected calendar year quantity. If the exclusion results in no potential violation of the BWON rule, then Wood River will not be required to implement corrective measures (i.e. a Compliance Assurance Plan).

### 6.3 COMPLIANCE ASSURANCE PLAN

If Wood River exceeds 1.5 Mg of benzene waste for a given quarter, the reason(s) for the occurrence cannot be identified, and Wood River cannot state that it does not expect the reason(s) to reoccur, then the Refinery will submit a



Compliance Assurance Plan. The Compliance Assurance Plan will be submitted to EPA for approval no later than 60 days after the end of the calendar quarter in which the exceedance occurred. The Compliance Assurance Plan will include (in accordance with Section N, Paragraph 217 of the Consent Decree):

- Identification of the causes of the potentially-elevated benzene quantities
- Corrective actions that will be taken or plans to ensure that the cause or causes will not reoccur
- The schedule of actions that will be taken to ensure that the Refinery complies with the BWON regulation for the calendar year

Wood River will implement the Plan unless EPA disapproves.

#### **6.4 THIRD-PARTY ASSISTANCE**

If analytical results indicate that the quarterly uncontrolled benzene quantity for two successive quarters equals or exceeds 1.5 Mg, or the projected annual uncontrolled benzene quantity exceeds 6 Mg and Wood River cannot identify the cause of the increased benzene contribution and cannot state that it does not expect the cause to reoccur, then the Refinery shall retain a third-party contractor during the following third calendar quarter to undertake a BWON study and compliance review. Wood River will submit the third-party study results to the EPA within 90 days of receipt of the third-party study, as well as a plan and schedule for remedying any deficiencies identified in the third-party study and compliance review. Wood River will implement the Plan unless EPA disapproves.

#### **6.5 SAMPLING PLAN UPDATE**

If changes in process, operations, or other factors lead Wood River to conclude that the Plan no longer provides an accurate basis for estimating the Refinery's quarterly or annual benzene quantity, then Wood River will submit a Revised Plan for EPA approval no later than 90 days after it is determined the original Plan no longer provides an accurate measure of uncontrolled benzene waste. Process changes include, but are not limited to, new construction, process elimination, and process alterations. When new construction occurs, benzene-containing waste streams will be evaluated for BWON applicability. If a process is eliminated, then those waste streams affected by the elimination will no longer be sampled. If a process is altered, then those waste streams affected by the alteration will be evaluated for sampling applicability with respect to the Consent Decree. Additionally, the sample frequency for non-routine sample locations may be altered. Wood River will implement the Revised Plan in the first full calendar quarter after submittal. Wood River will continue to implement the Revised Plan unless the EPA disapproves the Revised Plan.



Up to 2 years after the implementation of the Plan, the Refinery may submit a request for approval to EPA to revise the Plan, including the sampling frequency for non-routine samples. Wood River will not implement any proposed revisions until the Revised Plan is approved.

## TABLES

Table 1. Consent Decree Sampling Locations, ConocoPhillips Company, Wood River Refinery, Roxana, Illinois

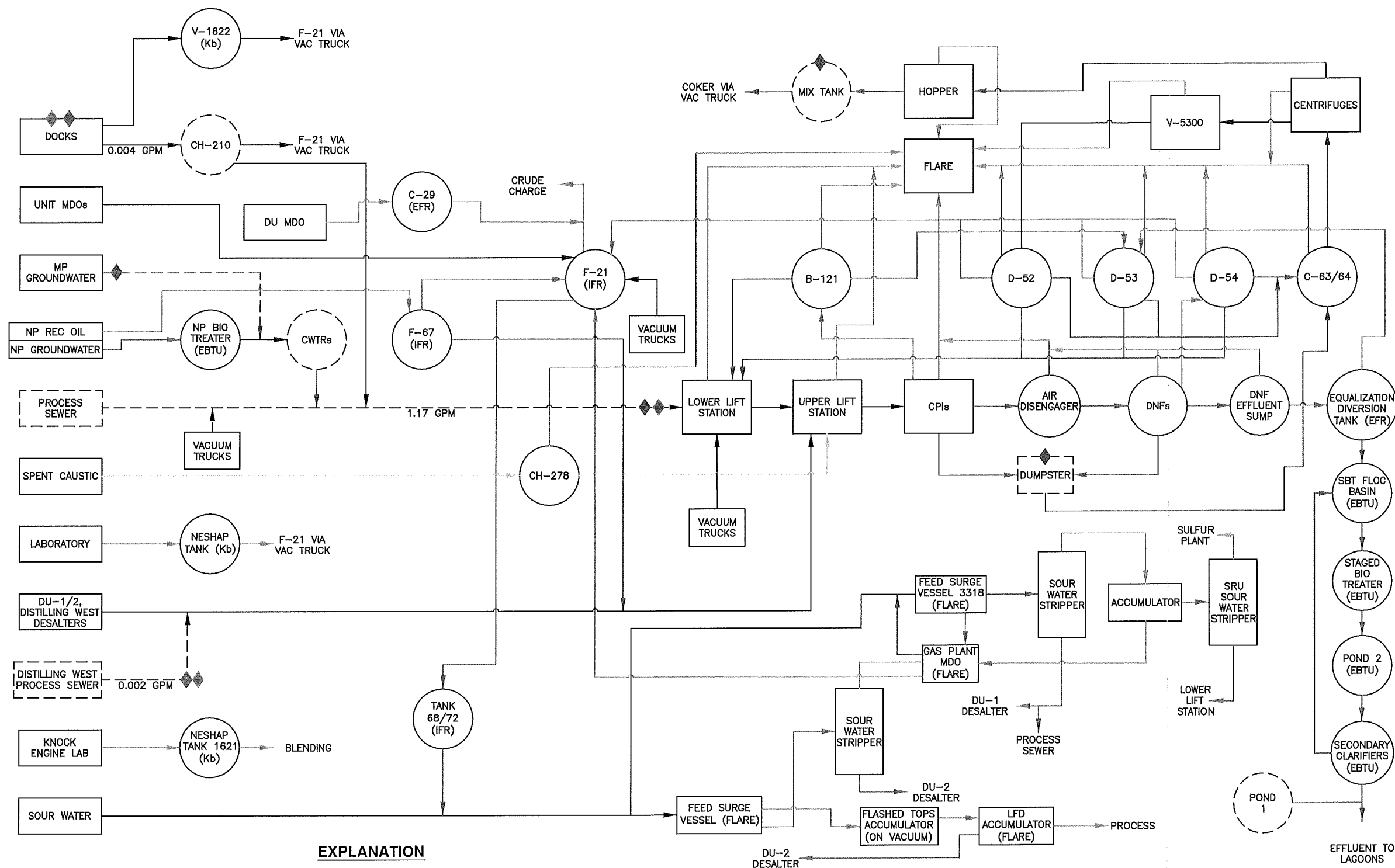
Sample Description	Sample Location	Phase Collected	Type	Sampling Method	Flow Rate Method
Dock Sumps / CH-210	Tank CH-210	HC/Water	End of Line	Grab	Instantaneous flow measurement / Process knowledge / Transfer records
MP (Main Plant) Groundwater	Well Pump Discharge	HC/Water	End of Line	Grab	Instantaneous flow measurement / Process knowledge / Transfer records
DW Process Sewer Sump	DW Process Sewer Sump Effluent	HC/Water	End of Line	Grab	Instantaneous flow measurement / Process knowledge / Transfer records
Lower Lift Station	Pump Discharge to the Upper Lift Station	HC/Water	End of Line	Grab	Instantaneous flow measurement / Process knowledge / Transfer records
Mix Tank	Mix Tank	HC/Water	End of Line	Grab	Process knowledge / Transfer records
Dumpster	Dumpster	HC/Water	End of Line	Grab	Process knowledge / Transfer records
SRC Column Water Boot (BEU)	SRC Water Boot Effluent	Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Surge Drum and Charge Pump Sample Station (CR3)	Surge Drum and Charge Pump Sample Station (CR3) Effluent	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Sour Water Stripper Bottoms (CGP-LOT)	Sour Water Stripper Bottoms (CGP-LOT) Effluent	Water	>0.05 Mg	Cooler	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Outlet Sample Bleeder Sample Station (CGP-LOT)	Outlet Sample Bleeder Sample Station (CGP-LOT) Effluent	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Sample Bleeder Sample Station (CGP-LOT)	Sample Bleeder Sample Station (CGP-LOT) Effluent	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Second Stage Triline Sample (DU1)	Second Stage Triline Sample (DU1) Effluent	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews


Table 1. Consent Decree Sampling Locations, ConocoPhillips Company, Wood River Refinery, Roxana, Illinois

Sample Description	Sample Location	Phase Collected	Type	Sampling Method	Flow Rate Method
First Stage Triline Sample (DU1)	First Stage Triline Sample (DU1) Effluent	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Mixed Crude Desalter Triline Samples (DU2)	Mixed Crude Desalter Triline Samples (DU2)	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Distilling West Desalter (1841) Triline	Distilling West Desalter (1841) Triline	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Distilling West Desalter (1840) Triline	Distilling West Desalter (1840) Triline	HC/Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Sour Water Stripper Bottoms (Environmental Operations)	Sour Water Stripper Bottoms (Environmental Operations)	Water	>0.05 Mg	Cooler	Instantaneous flow measurement / Process knowledge / Operation personnel interviews
Miscellaneous Vacuum Truck Hose Drillage	F21 Sump	HC/Water	>0.05 Mg	Grab	Process knowledge / Operation personnel interviews / Transfer records
Gasoline Sampling (Motor Laboratory)	Pipeline Sump	HC/Water	>0.05 Mg	Grab	Process knowledge / Operation personnel interviews
Dock Waste Permits (Dock)	CH-210	HC/Water	>0.05 Mg	Grab	Process knowledge / Operation personnel interviews / Transfer records
MP Well 83 (Spills and Miscellaneous Waste Streams)	Well Pump Discharge	Water	>0.05 Mg	Grab	Instantaneous flow measurement / Process knowledge
Solid Waste	Dumpster	HC/Water	>0.05 Mg	Grab	Process knowledge / Transfer records

## FIGURES





 <p>Trihydro CORPORATION 1252 Commerce Drive Laramie, Wyoming 82070 www.trihydro.com (P) 307/745.7474 (F) 307/745.7729</p>	<b>FIGURE 1</b>			
	<b>WASTE/SLOP/OFF-SPEC OIL MANAGEMENT SCHEMATIC</b>			
	<b>CONOCOPHILLIPS WOOD RIVER, ILLINOIS</b>			
Drawn By: REP	Checked By: RA	Scale: NONE	Date: 6/2/06	File: 436WWSOS_WOODRIVER